5. COMBUSTION SOURCES OF CDD/CDF: OTHER HIGH TEMPERATURE SOURCES

5.1. CEMENT KILNS AND LIGHTWEIGHT AGGREGATE KILNS

This section addresses CDD/CDF emissions from portland cement kilns. These facilities use high temperatures to convert mineral feedstocks into portland cement and other types of construction materials. For purposes of this analysis, cement kilns have been subdivided into two categories, those that burn hazardous waste and those that do not, and these two subcategories are further divided into kilns with inlet APCD temperatures above and below 450°F. The following subsections describe cement kiln technology, the derivation of TEQ emission factors for cement kilns that burn hazardous waste as supplemental fuel and those that do not, and the derivation of annual TEQ air emissions (g/yr) for 1995 and 1987.

Lightweight aggregate kilns that combust liquid hazardous wastes are not addressed in detail in this report. Only 5 of the more than 36 lightweight aggregate kilns in the United States combust hazardous waste. Those facilities are estimated to have emitted 3.3 g I-TEQ_{DF} to air in 1990 (Federal Register, 1998b) and 2.4 g I-TEQ_{DF} in 1997 (Federal Register, 1999b). These estimates are used in this report as the estimates for reference years 1987 and 1995, respectively. Regulations issued by EPA under the Clean Air Act (CAA) and Resource Conservation and Recovery Act (RCRA) in 1999 (Federal Register, 1999b) are expected to reduce those emissions to 0.4 g I-TEQ_{DF} within the next 3 to 4 years.

5.1.1. Process Description of Portland Cement Kilns

In the United States, the primary cement product is portland cement. Portland cement is a fine, grayish powder consisting of a mixture of four basic materials: lime, silica, alumina, and iron compounds. Cement production involves heating (pyroprocessing) the raw materials to a very high temperature in a rotary (rotating) kiln to induce chemical reactions that produce a fused material called clinker. The cement clinker is then ground into a fine powder and mixed with gypsum to form the portland cement. The cement kiln is a large, steel, rotating cylindrical furnace lined with refractory material. The kiln is aligned on a slight angle, usually a slope of 3 to 6°. This allows the materials to pass through the kiln by gravity. The upper end of the kiln, known as the “cold” end, is where the

raw materials, or meal, are generally fed into the kiln. Midpoint injection is practiced at some facilities. The lower end of the kiln is known as the hot end. The hot end is where the combustion of primary fuels (usually coal and petroleum coke) transpires to produce a high temperature. The cement kiln is operated in a counter-current configuration, in which the hot combustion gases are convected up through the kiln while the raw materials pass down toward the lower end. The kiln rotates about 50 to 70 revolutions per hour, and the rotation induces mixing and the forward progress of mixed materials. As the meal moves through the cement kiln and is heated by the hot combustion gases, water is vaporized and pyroprocessing of materials occurs.

When operating, the cement kiln can be viewed as consisting of three temperature zones necessary to produce cement clinker. Zone 1 is at the upper end of the kiln where the raw meal is added. Temperatures in this zone typically range from ambient up to 600°C. In this area of the kiln, moisture is evaporated from the raw meal. The second thermal zone is known as the calcining zone. Calcining occurs when the hot combustion gases from the combustion of primary fuels dissociates calcium carbonate from the limestone to form calcium oxide. In this region of the kiln, temperatures range from 600°C to 900°C. Zone 3 is known as the burning or sintering zone. The burning zone, the lowest region of the kiln, is the hottest. Here temperatures in excess of 1,500°C induce the calcium oxide to react with silicates, iron, and aluminum in the raw materials to form cement clinker. The formation of clinker actually occurs close to the combustion of primary fuel. The chemical reactions that occur in Zone 3 are referred to as pyroprocessing.

The cement clinker, which leaves the kiln at the hot end, is a gray, glass-hard material consisting of dicalcium silicate, tricalcium silicate, calcium aluminate, and tetracalcium aluminoferrite. At this point, the clinker is about 1,100°C. The hot clinker is then dumped onto a moving grate, where it cools as it passes under a series of cool air blowers. Once cooled to ambient temperature, the clinker is ground into a fine powder and mixed with gypsum to produce the portland cement product.

Cement kilns can be either wet or dry processes. In the wet process, the raw materials are ground and mixed with water to form a slurry, which is fed into the kiln through a pump. This is an older process. A greater amount of heat energy is needed in the wet process than in other types of kilns. These kilns consume about 5 to 7 trillion BTUs per ton of clinker product to evaporate the additional water.

In the dry process, a preheater is used to dry the raw meal before it enters the kiln. A typical preheater consists of a vertical tower containing a series of cyclone-type vessels. Raw meal is added at the top of the tower, and hot exhaust gases from the kiln operation preheat the meal, thus lowering the fuel consumption of the kiln. Dry kilns are now the most popular cement kiln type. Portland cement clinker production in the United States is estimated to have been 67.6 billion kg in 1995 and 52 billion kg in 1987 (U.S. Department of Commerce, 1996).

5.1.2. Cement Kilns That Burn Hazardous Waste

The high temperatures achieved in cement kilns make the kilns an attractive technology for combusting hazardous waste as supplemental fuel. Sustaining the relatively high combustion temperatures (1,100°C to 1,500°C) that are needed to form cement clinker requires the burning of a fuel with a high energy output. Therefore, coal or petroleum coke is typically used as the primary fuel source. Because much of the cost of operating the cement kiln at high temperatures is associated with the consumption of fossil fuels, some cement kiln operators have elected to burn hazardous liquid and solid waste as supplemental fuel. Currently about 75 percent of the primary fuel is coal. Organic hazardous waste may have a similar energy output as coal (9,000 to 12,000 Btu/lb for coal). The strategy of combusting the waste as supplemental fuel is to offset the amount of coal/coke that is purchased and burned by the kiln. The operator may charge a disposal fee to the waste generator for the right to combust the hazardous waste at the kiln, which also offsets the cost of kiln operation. Much of the high-energy and ignitable wastes primarily comprise such diverse substances as waste oils, spent organic solvents, sludges from the paint and coatings industry, waste paints and coatings from auto and truck assembly plants, and sludges from the petroleum refining industry (Greer et al., 1992).

The conditions inherent in the cement kiln mimic conditions of hazardous waste incineration. For example, the gas residence time in the burning zone is typically three seconds while at temperatures in excess of 1,500°C (Greer et al., 1992). The method of introducing liquid and solid hazardous waste into the kiln is a key factor to the complete consumption of the waste during the combustion of the primary fuel. Liquid hazardous waste is either injected separately or blended with the primary fuel (coal). Solid waste is mixed and burned along with the primary fuel. Trial burns have consistently shown that

99.99 to 99.9999 percent destruction and removal efficiencies for the very stable organic wastes can be achieved in cement kilns (Greer et al., 1992). However, although the combustion of hazardous waste as supplemental or substitute fuel does have apparent advantages, only 16 percent of the portland cement kilns (34 of 212 kilns) in the United States combusted hazardous waste in 1995 (Federal Register, 1996b). Other types of supplemental fuel used by these facilities include automobile tires, used motor oil, sawdust, and scrap wood chips.

5.1.3. Air Pollution Control Devices Used on Cement Kilns

The pyroprocessing of raw meal in a cement kiln produces fine particulates, referred to as cement kiln dust. Cement kiln dust is collected and controlled with fabric filters or electrostatic precipitators, or both. Acid gases such as SO_2 can be formed during pyroprocessing of the sulfur-laden minerals, but the minerals have high alkalinity, which neutralizes SO_2 gases. Most particulate matter (PM) control devices used at cement kilns in 1995 and 1987 were considered to be hot-side control devices. A hot-sided control device is one that operates at flue gas temperatures above 450°F (some EPA rules use different definitions for hot-sided control devices for different industries).

Reducing the flue gas temperature in the PM control device is one factor shown to have a significant impact on limiting dioxin formation and emissions at cement kilns (U.S. EPA, 1997d). Recent emissions testing at a portland cement kiln showed that CDD/CDFs were almost entirely absent at the inlet to a hot-sided ESP, but CDDs and CDFs were measured at the exit (U.S. EPA, 1997d), showing conclusively that dioxins were formed within the hot-sided ESP. Reducing the flue gas temperature in the PM control device to below 450°F has been shown to substantially limit CDD/CDF formation at cement kilns. Lower temperatures are believed to prevent the post-combustion catalytic formation of CDD/CDFs. Consequently a number of cement kilns have added flue gas quenching units upstream of the APCD to reduce the inlet APCD temperature, thereby reducing CDD/CDF stack concentrations. A quenching unit usually consists of a water spray system within the flue duct. Thus, current CDD/CDF emissions from cement kilns are believed to be substantially lower than CDD/CDF emissions in 1987 and 1995; EPA/OAQPS estimated emissions to be 13.1 g I-TEQ_{DF} in 1997 (Federal Register, 1999b).

5.1.4. CDD/CDF Emission Factors for Cement Kilns

For purposes of deriving emission factors, the general strategy used in this document is to consider subdividing each source category on the basis of design and operation. However, cement kilns are relatively uniform in terms of kiln design, raw feed material, temperatures of operation, and APCDs. Therefore, no subdivisions were made on these bases. An important potential difference among kilns, however, is whether or not hazardous waste is burned as a supplementary fuel. The source emissions database used in this report contains CDD/CDF emissions data for 16 cement kilns burning hazardous waste and 15 cement kilns not burning hazardous waste as reported in U.S. EPA (1996c). The majority of stack emissions data from cement kilns burning hazardous waste were derived during trial burns and may overestimate the CDD/CDF emissions that most kilns achieve during normal operations. Stack emissions data from kilns not burning hazardous waste were derived from testing during normal operations. The average TEQ emission factors are 20.91 ng I-TEQ_{DF}/kg clinker produced (22.48 ng TEQ_{DF}-WHO_{98}/kg clinker) and 0.27 ng I-TEQ_{DF}/kg clinker produced (0.29 ng TEQ_{DF}-WHO_{98}/kg clinker) for cement kilns burning and not burning hazardous waste, respectively. Accordingly, the average emission factor for kilns burning hazardous waste is about 90 times greater than that for kilns not burning hazardous waste. As discussed in Section 5.1.6 (Cement Kiln Dust), a comparison of CDD/CDF concentrations in cement kiln dust samples from cement kilns burning and not burning hazardous waste shows a similar relationship (i.e., the cement kiln dust from kilns burning hazardous waste had about 100 times higher CDD/CDF TEQ concentration than dust from kilns not burning hazardous waste).

Although the average emission factors for the two groups of kilns differ substantially, the emission factors for individual kilns in the two groups overlap. Therefore, other aspects of the design and operation of the kilns are likely to be affecting CDD/CDF emissions, particularly the temperature of the APCD equipment as discussed in Section 5.1.3.

Previous attempts to understand this issue through parametric testing of cement kilns have yielded mixed results. EPA conducted a limited comparison of CDD/CDF TEQ stack gas concentrations (ng TEQ/dscm) between cement kilns burning hazardous wastes and not burning hazardous wastes (U.S. EPA, 1997d). Those comparisons were made at 14 cement kilns. Operating conditions (e.g., APCD temperature), with the exception of the

fuel being burned, were the same or similar for each set of comparisons. Baseline conditions used coal as the only primary fuel. The results of these comparisons showed the following:

- Seven kilns in which the baseline (i.e., no combustion of hazardous waste) CDD/CDF TEQ stack gas concentrations were about the same as that for the burning of hazardous wastes.
- Two kilns in which the baseline CDD/CDF I-TEQ_{DF} stack gas concentrations were about double that for the burning of hazardous wastes.
- Five kilns in which the hazardous waste CDD/CDF I-TEQ_{DF} stack gas concentrations were substantially greater (from 3 to 29 times greater) than that for the baseline operating conditions.

Subsequently, EPA/ORD conducted analyses of the available emissions data to evaluate, on a congener-specific basis, whether there were significant differences in emission factors between (a) kilns burning hazardous waste and those not burning hazardous waste; (b) kilns with APCD inlet temperatures greater than 450°F and those with temperature less than 450°F; (c) hazardous waste burning and non–hazardous waste burning facilities with APCD inlet temperatures greater than 450°F; (d) hazardous waste burning and non–hazardous waste burning facilities with APCD inlet temperatures less than 450°F; (e) hazardous waste burning facilities with APCD inlet temperatures less than or greater than 450°F; and (f) non–hazardous waste burning facilities with APCD inlet temperatures less than or greater than 450°F. The results of all analyses showed significant differences in the sample mean values ($p < 0.05$).

Currently no satisfactory explanation exists for the apparent differences in the emission factors. Given the strong empirical evidence that real differences may exist, EPA/ORD has decided to treat the kilns burning hazardous waste separately from those not burning hazardous waste for the purposes of developing a CDD/CDF emissions inventory, and to subdivide the hazardous waste burning category into subcategories by APCD inlet temperature (i.e., less than 450°F or greater than 450°F). APCD inlet temperature data were available for 88 test runs at 14 cement kilns. The number of test runs conducted at individual kilns ranged from 1 to 26. Each test run was treated as an individual facility and each was classified according to APCD inlet temperature and whether or not hazardous

waste was burned. The emission factor (EF) for each cement kiln test run was calculated using Equation 5-1.

$$EF_{ck} = \frac{C \times F_v}{I_{cl}} \qquad \text{(Eq. 5-1)}$$

Where:

EF_{ck} = Cement kiln emission factor (burning or not burning hazardous waste), (ng TEQ/kg of clinker produced)

C = TEQ or CDD/CDF concentration in flue gases (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2)

F_v = Volumetric flue gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2)

I_{cl} = Average cement kiln clinker production rate (kg/hr)

After developing the emission factor for each cement kiln test run, the overall average congener-specific emission factor was derived for all test runs in each subcategory using Equation 5-2 below.

$$EF_{avgCK} = \frac{EF_{CK_1} + EF_{CK_2} + EF_{CK_3} + \ldots\ldots\ldots + EF_{CKN}}{N} \qquad \text{(Eq. 5-2)}$$

Where:

EF_{avgCK} = Average emission factor of tested cement kilns burning hazardous waste as supplemental fuel and with APCD inlet temperatures either greater than or less than 450°F (ng TEQ/kg clinker)

N = Number of cement kiln test runs

The average emission factors representing these categories of cement kilns are summarized in Table 5-1. Because the same test reports were used, the emission factors are the same

for both the 1995 and 1987 reference years. Average congener and congener group profiles for cement kilns burning hazardous waste are presented in Figure 5-1 and for cement kilns not burning hazardous wastes in Figure 5-2.

5.1.5. National Estimates of CDD/CDF Emissions from Cement Kilns

Non–hazardous waste burning cement kilns produced 61.3 billion kg of cement clinker in 1995 (Heath, 1995). Since a total of 67.6 billion kg of cement clinker were produced in the United States in 1995 (U.S. DOC, 1996), it follows that cement kilns burning hazardous waste produced 6.3 billion kg of clinker, or 9.3 percent of the clinker produced. In 1987, approximately 52 billion kg of cement clinker were produced (U.S. DOC, 1996). If it is assumed that 9.3 percent of this total clinker production was from kilns burning hazardous waste, then about 4.8 billion kg of clinker were produced in hazardous waste burning kilns in 1987. These activity level estimates are given a high confidence rating for 1995 because they are based on recent survey data, but a medium rating for 1987 because of uncertainty concerning the proportion produced by hazardous waste burning kilns (U.S. EPA, 1996c).

The TEQ emission factors are given a low confidence rating for all subcategories. The emission factor for non–hazardous waste burning kilns was given a low rating because test data were available for only 15 of 178 facilities. The tested facilities may not be representative of routine CDD/CDF emissions from all kilns not burning hazardous waste. Although a higher percentage of the kilns burning hazardous waste (with reported APCD temperature data) had been tested (10 out of 34; eight with APCD inlet temperatures greater than 450°F and two with temperatures less than 450°F), greater uncertainty exists about whether the emissions are representative of normal operations because trial burn procedures were used. Accordingly, a low confidence rating was also assigned to the estimated emissions factors for kilns burning hazardous waste.

National estimates of CDD/CDF air emissions (grams TEQ per year) from all portland cement kilns operating in 1995 and 1987 were made by multiplying the average TEQ emission factors by an estimate of the annual activity level (cement clinker produced) for each of the three subcategories (hazardous waste burning kilns with APCD inlet temperatures greater than 450°F, hazardous waste burning kilns with APCD inlet temperatures less than 450°F, and kilns not burning hazardous waste).

Of the 10 hazardous waste burning kilns with APCD temperature data, 8 facilities (80 percent) had APCD inlet temperatures greater than 450°F; 2 (20 percent) had APCD inlet temperatures less than 450°F. If it is assumed that the percentages of hazardous waste burning kilns less than and greater than 450°F represent the actual distribution of activity level in the industry, then one can use these percentages, coupled with the TEQ emission factors presented in Table 5-1 and the activity levels established at the beginning of this section, to calculate the annual national TEQ emission estimates shown below.

Reference Year 1995

Category	TEQ Emission Factor (ng/kg clinker)		Activity Level (billion kg clinker/yr)	Annual TEQ Emission (g/yr)	
	I-TEQ_{DF}	TEQ_{DF}-WHO_{98}		I-TEQ_{DF}	TEQ_{DF}-WHO_{98}
HW >450°F	28.58	30.70	5.04	144.0	154.7
HW <450°F	1.04	1.11	1.26	1.3	1.4
NHW	0.27	0.29	61.3	16.6	17.8
TOTAL			67.6	162	174

Reference Year 1987

Category	TEQ Emission Factor (ng/kg clinker)		Activity Level (billion kg clinker/yr)	Annual TEQ Emission (g/yr)	
	I-TEQ_{DF}	TEQ_{DF}-WHO_{98}		I-TEQ_{DF}	TEQ_{DF}-WHO_{98}
HW >450°F	28.58	30.70	3.8	108.6	116.7
HW <450°F	1.04	1.11	1.0	1.0	1.1
NHW	0.27	0.29	47.2	12.7	13.7
TOTAL			52.0	122	132

5.1.6. Recent EPA Regulatory Activities

In May 1999, EPA promulgated national emission standards under the authority of the Clean Air Act for hazardous air pollutants (including CDD/CDFs) for new and existing cement kilns not burning hazardous waste (Federal Register, 1999a). EPA/OAQPS expects

this rule to reduce emissions of I-TEQ_{DF} by existing and new facilities by 36 percent over the next 5 years (i.e., from an estimated 44 g I-TEQ_{DF} in 1997 to 29 g I-TEQ_{DF} per year).

In July 1999, EPA promulgated national emission standards under the joint authority of the Clean Air Act and the Resource Conservation and Recovery Act for hazardous air pollutants (including CDD/CDFs) for hazardous waste combustion facilities (including cement kilns burning hazardous waste). Within the next 3 to 4 years under the final emissions limits, emissions of I-TEQ_{DF} by hazardous waste burning facilities are projected by EPA/OAQPS to be reduced by 40 percent (i.e., from an estimated 13.1 g I-TEQ_{DF} in 1997 to 7.7 g I-TEQ_{DF} per year) (Federal Register, 1999b).

5.1.7. Cement Kiln Dust

EPA characterized cement kiln dust (CKD) in a Report to Congress (U.S. EPA, 1993g). The report was based in part on a 1991 survey of cement manufacturers conducted by the Portland Cement Association (PCA). Survey responses were received from 64 percent of the active cement kilns in the United States. On the basis of the survey responses, EPA estimated that in 1990 the U.S. cement industry generated about 12.9 million metric tons of gross CKD and 4.6 million metric tons of "net CKD," of which 4.2 million metric tons were land disposed. The material collected by the APCD system is called "gross CKD" (or "as generated" CKD). The gross CKD is either recycled back into the kiln system or is removed from the system for disposal (i.e., "net CKD" or "as managed" CKD) (U.S. EPA, 1993g).

In support of the Report to Congress, EPA also conducted sampling and analysis during 1992 and 1993 of CKD and clinker. The purposes of the sampling and analysis efforts were to: (1) characterize the CDD/CDF content of clinker and CKD; (2) determine the relationship, if any, between the CDD/CDF content of CKD and the use of hazardous waste as fuel; and (3) determine the relationship, if any, between the CDD/CDF content of CKD and the use of wet process versus dry process cement kilns (U.S. EPA, 1993g).

Clinker samples were collected from five kilns not burning hazardous waste and six kilns burning hazardous waste (U.S. EPA, 1993g). CDD/CDFs were not detected in any cement kiln clinker samples. Tetra- through octa-chlorinated CDDs and CDFs were detected in the gross CKD samples obtained from 10 of the 11 kilns and in the net CKD samples obtained from 8 of the 11 kilns. The CDD/CDF content of gross CKD ranged from

0.008 to 247 ng I-TEQ$_{DF}$/kg and from 0.045 to 195 ng I-TEQ$_{DF}$/kg for net CKD. Analyses for seven PCB congeners were also conducted, but no congeners were detected in any clinker or CKD sample. The mean CDD/CDF concentrations in net CKD generated by the kilns burning hazardous waste are higher (35 ng I-TEQ$_{DF}$/kg) than in net CKD generated by the facilities not burning hazardous waste (3.0E-02 ng I-TEQ$_{DF}$/kg). These calculations of mean values treated nondetected values ("nondetects") as zero. If the nondetected values had been excluded from the calculation of the means, the mean value for net CKD from kilns burning hazardous waste would increase by a factor of 1.2, and the mean value for net CKD from kilns not burning hazardous waste would increase by a factor of 1.7. One sampled kiln had a net CKD TEQ concentration more than two orders of magnitude greater than the TEQ levels found in samples from any other kiln. If this kiln was considered atypical of the industry (U.S. EPA, 1993g) and was not included in the calculation, then the mean net CKD concentration for hazardous waste burning kilns decreases to 2.9 ng I-TEQ$_{DF}$/kg.

All CKD is normally disposed of in engineered landfills and is consequently not categorized as an environmental release as defined in this emission inventory. The amount of CDD/CDF associated with these materials is calculated for informational purposes. The estimate of land-disposed CKD from the 1991 PCA survey (4.2 million metric tons per year; basis year is 1990) was divided among kilns that burn hazardous waste (34 kilns) and those that do not (178 kilns) on the basis of the number of kilns in each category. The average TEQ concentration in the net CKD from kilns burning hazardous waste (including the high value discussed above) was 35 ng I-TEQ$_{DF}$/kg. For kilns that do not burn hazardous waste, the average concentration in the net CKD was 3.0E-02 ng I-TEQ$_{DF}$/kg. Multiplying these average concentrations by the estimated annual net CKD production yields 24 g I-TEQ$_{DF}$/yr for kilns burning hazardous waste and 0.1 g I-TEQ$_{DF}$/yr for kilns not burning hazardous waste, a total of 24.1 g I-TEQ$_{DF}$/yr for all kilns in 1990.

EPA is currently developing cement kiln dust storage and disposal requirements (Federal Register, 1999b).

5.2. ASPHALT MIXING PLANTS

Asphalt consists of an aggregate of gravel, sand, and filler mixed with liquid asphalt cement or bitumen. Filler typically consists of limestone, mineral stone powder, and

sometimes ash from power plants and municipal waste combustors. The exact composition of an asphalt formulation depends on how it will be used. The aggregate typically constitutes over 92 percent by weight of the total asphalt mixture. The components of the aggregate are dried, heated to a temperature ranging from 275 to 325°F, and then mixed and coated with the bitumen at an asphalt mixing installation. "Old" asphalt (i.e., asphalt from dismantled bridges and roads) can be heated and disaggregated to its original components and reused in the manufacture of new asphalt (U.S. EPA, 1996i).

No data are available on levels of CDD/CDF emissions, if any, from U.S. asphalt mixing operations. However, limited data are available for facilities in The Netherlands and Germany.

Bremmer et al. (1994) reported the CDD/CDF emissions factor for an asphalt mixing plant in The Netherlands at 47 ng I-TEQ_{DF} per metric ton of produced asphalt. No congener-specific emission factors were reported. The facility they tested heated old asphalt to about 150°C in an individual recycling drum with flue gases that were mixed with ambient air and heated to a temperature of 300–400°C. Parallel to this recycling drum, the main drum dried and heated the aggregate (sand and gravel/granite chippings) to a temperature of about 220°C. The flue gases leaving the recycling drum were led along the main burner of the main drum for incineration. The old asphalt, the minerals from the main drum, and new bitumen from a hot storage tank (about 180°C) were mixed in a mixer to form new asphalt. Natural gas fueled the tested facility during the sample collection period and used old asphalt as 46 percent of the feed. The facility's APCD system consisted of cyclones and a fabric filter.

Umweltbundesamt (1996) reported lower emission factors for three tested facilities in Germany that were also equipped with fabric filters. These three facilities were fueled by oil or butane gas and used old asphalt at rates ranging from 30 to 60 percent of the feed. The emission factors calculated from the stack gas concentrations, gas flow rates, and hourly throughputs for these three facilities were 0.2, 3.5, and 3.8 ng I-TEQ_{DF}/metric ton of asphalt produced.

Approximately 25 million metric tons of asphalt bitumen were produced in the United States in 1992. An identical quantity was produced in 1990 (U.S. DOC, 1995a). Bitumen constitutes approximately 5 percent by weight of finished paving asphalt (Bremmer

et al., 1994). Thus, an estimated 500 million metric tons of paving asphalt are produced in the United States annually.

Because there are no direct measurements of CDD/CDF emissions from U.S. asphalt plants and because of uncertainties regarding the comparability of U.S. and Dutch asphalt plant technologies and feed materials, no national emission estimate for this category is proposed at this time. However, a preliminary estimate of the potential magnitude of annual TEQ emissions for U.S. production of asphalt can be obtained by averaging the emission factors for the four facilities reported by Bremmer et al. (1994) and Umweltbundesamt (1996). Applying this average emission factor (i.e., 14 ng I-TEQ_{DF}/metric ton of asphalt produced) to the activity level of 500 million metric tons of paving asphalt produced annually yields an annual emission of 7 g I-TEQ_{DF}/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions. Congener-specific results were not reported in either report. Therefore, TEQ_{DF}-WHO_{98} estimates could not be calculated.

5.3. PETROLEUM REFINING CATALYST REGENERATION

Regeneration of spent catalyst from the reforming process at petroleum refineries is a potential source of CDDs and CDFs according to limited testing conducted in the United States (Amendola and Barna, 1989; Kirby, 1994), Canada (Maniff and Lewis, 1988; Thompson et al., 1990), and The Netherlands (Bremmer et al., 1994). This section summarizes the catalyst regeneration process, relevant studies performed to date, and the status of EPA regulatory investigations of this source.

Catalytic reforming is the process used to produce high-octane reformates from lower octane reformates for blending of high-octane gasolines and aviation fuels. The reforming process occurs at high temperature and pressure and requires the use of a platinum or platinum/rhenium catalyst. During the reforming process, a complex mixture of aromatic compounds, known as coke, is formed and deposited onto the catalyst. As coke deposits onto the catalyst, its activity is decreased. The high cost of the catalyst necessitates its regeneration. Catalyst regeneration is achieved by removing the coke deposits via burning at temperatures of 750 to 850°F and then reactivating the catalyst at elevated temperatures (850 to 1,000°F) using chlorine or chlorinated compounds (e.g.,

methylene chloride, 1,1,1-trichloroethane, and ethylene dichloride). Burning of the coke produces flue gases that can contain CDDs and CDFs along with other combustion products. Because flue gases, if not vented directly to the atmosphere, may be scrubbed with caustic or water, internal effluents may become contaminated with CDD/CDFs (Kirby, 1994; SAIC, 1994).

There are three basic catalyst regeneration processes used: semi-regenerative, cyclic, and continuous. During the semi-regenerative process, the entire catalytic reformer is taken off-line. In the cyclic process, one of two (or more) reforming reactors is taken off-line for catalyst regeneration; the remaining reactor(s) remains on-line so that reforming operations continue. In the continuous process, aged catalyst is continuously removed from one or more on-line stacked or side-by-side reactors, regenerated in an external regenerator, and then returned to the system; the reforming system, consequently, never shuts down (SAIC, 1994).

In 1988, the Canadian Ministry of the Environment detected concentrations of CDDs in an internal waste stream of spent caustic in a petroleum refinery that ranged from 1.8 to 22.2 μgL, and CDFs ranging from 4.4 to 27.6 μg/L (Maniff and Lewis, 1988). The highest concentration of 2,3,7,8-TCDD was 0.0054 μg/L. CDDs were also observed in the refinery's biological sludge at a maximum concentration of 74.5 μg/kg, and CDFs were observed at a maximum concentration of 125 μg/kg. The concentration of CDD/CDFs in the final combined refinery plant effluent was below the detection limits.

Amendola and Barna (1989) reported detecting trace levels of hexa- to octa-CDDs and CDFs in untreated wastewaters (up to 2.9 pg I-TEQ_{DF}/L) and wastewater sludges (0.26 to 2.4 ng I-TEQ_{DF}/kg) at a refinery in Ohio. The levels of detected total CDD/CDFs in the wastewater and sludge were much lower (< 3 ng/L and < 1 μg/kg, respectively) than the levels reported by Maniff and Lewis (1988). No CDD/CDFs were detected in the final treated effluent (i.e., less than 0.2 ng I-TEQ_{DF}/L). The data collected in the study were acknowledged to be too limited to enable identifying the source(s) of the CDD/CDFs within the refinery. Amendola and Barna (1989) also present in an appendix to their report the results of analyses of wastewater from the catalyst regeneration processes at two other U.S. refineries. In both cases, untreated wastewaters contained CDDs and CDFs at levels ranging from high pg/L to low ng/L (results were reported for congener group totals, not

specific congeners). However, CDD/CDFs were not detected in the only treated effluent sample collected at one refinery.

Thompson et al. (1990) reported total CDD and CDF concentrations of 8.9 ng/m^3 and 210 ng/m^3, respectively, in stack gas samples from a Canadian petroleum refinery's reforming operation. They also observed CDDs and CDFs in the internal wash water from a scrubber of a periodic/cyclic regenerator in the pg/L to ng/L range.

Beard et al. (1993) conducted a series of benchtop experiments to investigate the mechanism(s) of CDD/CDF formation in the catalytic reforming process. A possible pathway for the formation of CDFs was found, but the results could not explain the formation of CDDs. Analyses of the flue gas from burning coked catalysts revealed the presence of unchlorinated dibenzofuran (DBF) in quantities up to 220 μg/kg of catalyst. Chlorination experiments indicated that DBF and possibly biphenyl and similar hydrocarbons act as CDF precursors and can become chlorinated in the catalyst regeneration process. Corrosion products on the steel piping of the process plant seem to be the most likely chlorinating agent.

In May 1994, EPA's Office of Water conducted a sampling and analytical study of catalyst regeneration wastewater for CDD/CDFs at three petroleum refining plants (Kirby, 1994). The study objectives were to determine the analytical method best suited for determining CDD/CDFs in refinery wastewater and to screen and characterize wastewater discharges from several types of reforming operations for CDD/CDFs. The report for this study (Kirby, 1994) also presented results submitted voluntarily to EPA by two other facilities. The sampled internal untreated wastewaters and spent caustics were found to contain a wide range of CDD/CDF concentrations, 0.1 pg I-TEQ_{DF}/L to 57.2 ng I-TEQ_{DF}/L. The study results also showed that 90 percent of the TEQ was contained in the wastewater treatment sludges generated during the treatment of wastewater and caustic from the regeneration process.

In 1995, EPA issued a notice of its proposed intent not to designate spent reformer catalysts as a listed hazardous waste under RCRA (Federal Register, 1995b). The final rule was issued in August 1998 (Federal Register, 1998a). The Agency's assessment of current management practices associated with recycling of reforming catalyst found no significant risks to human health or the environment. The Agency estimated that 94 percent of the approximately 3,600 metric tons of spent reformer catalyst sent off-site by

refineries are currently recycled for their precious-metal content. However, EPA made no determination of the "listability" of spent caustic residuals formed during regeneration of spent reforming catalyst. The Agency did identify as being possibly of concern potential air releases from the combustion of the reforming catalyst prior to reclamation. The Agency requested comments on (a) opportunities for removing dioxin prior to discharge of scrubber water into the wastewater treatment system; (b) opportunities to segregate this wastestream; and (c) potential health risks associated with insertion of dioxin-contaminated media back into the refinery process (such as the coker). In this proposed rulemaking, EPA also noted the possibility of dioxin releases to air during regeneration operations.

As part of its regulatory investigation under RCRA, EPA's OSW commissioned a study to analyze and discuss existing data and information concerning CDD/CDF formation in the treatment of catalytic reformer wastes. This report (SAIC, 1994) also identified potential process modifications that may prevent the formation of CDD/CDFs. SAIC (1994) concluded that, although the available data indicate that CDD/CDFs can be generated during the catalyst regeneration process, the available data indicate that CDD/CDF concentrations in treated wastewater and in solid waste are minimal. Releases to air could result from vented flue gases at some facilities. In addition, the CDD/CDFs formed could possibly be reintroduced into other refining operations (e.g., the coker) and resulting products.

In 1998, emissions from the caustic scrubber used to treat gases from the external regeneration unit of a refinery in California were tested (CARB, 1999). This facility uses a continuous regeneration process. The reactor is not taken off-line during regeneration; rather, small amounts of catalyst are continuously withdrawn from the reactor and are regenerated. The emissions from the regeneration unit are neutralized by a caustic scrubber before being vented to the atmosphere. The catalyst recirculation rate during the three tests ranged from 733 to 1,000 lbs/hr.

All 2,3,7,8-substituted CDD/CDFs were detected in each of the three samples collected. The average emission factors in units of ng/barrel of reformer feed are presented in Table 5-2. The congener profile is presented in Figure 5-3. The samples showed a wide range in concentrations of the CDD/CDF congeners (up to fivefold difference); however, the congener profile was consistent in all samples. The concentrations of the individual furan congener groups were always higher than the concentrations of the corresponding dioxin

congener group. The average I-TEQ_{DF} emission factor for these three tests is 3.04 ng TEQ/barrel and the average TEQ_{DF}-WHO_{98} is 3.18 ng TEQ/barrel.

In 1991, stack testing was performed on the exhaust from one of three semi-regenerative catalytic reforming units of a refinery in California (Radian, 1991b). A caustic solution is introduced to the exhaust to neutralize hydrochloric acid emissions from the catalyst beds prior to release to the atmosphere. The tested unit was considered to be representative of the other units. Each unit is periodically (approximately once per year) taken off-line so the catalyst beds can be regenerated. The tested unit has a feed capacity of 7,000 barrels per day. Approximately 59,500 pounds of catalyst were regenerated during the tested regeneration cycle, which tested for 62 hours.

The average emission factors for this facility (in units of ng/barrel of reformer feed) are presented in Table 5-2 and the congener profile is presented in Figure 5-3. The majority of the 2,3,7,8-substituted CDD congeners were not detected during testing. In contrast, the majority of the 2,3,7,8-substituted CDF congeners were detected. The average I-TEQ_{DF} emission factor (assuming not detected values are zero) is 1.01E-03 ng TEQ/barrel and the average TEQ_{DF}-WHO_{98} emission factor is 1.04E-03 ng TEQ/barrel. These values are three orders of magnitude less than the emission factor reported in CARB (1999). The calculation of these emission factors involved several assumptions: the unit is regenerated once per year; the unit operates at capacity (i.e., 7,000 barrels/day); and the facility operates 362 days per year.

The average of the two facility emission factors, 1.52 ng I-TEQ_{DF}/barrel of reformer feed (1.59 ng TEQ_{DF}-WHO_{98}/barrel), is assigned a low confidence rating. Only one continuous and only one semi-regenerative unit in the United States have been tested. Combined, these two facilities represent less than 1 percent of the catalytic reforming capacity in U.S. petroleum refineries in 1987 (3.805 million barrels per day) and in 1995 (3.867 million barrels per day) (EIA, 1997c). The average emission factor developed above assumes that emissions are proportional to reforming capacity; however, emission factors may be more related to the amount of coke burned, the APCD equipment present, or other process parameters.

The 1987 and 1995 national daily average catalytic reforming capacities in the United States were 3.805 and 3.867 million barrels per day (EIA, 1997c). If it is conservatively assumed that all units operated at full capacity in 1987 and 1995, then

applying the average emission factors of TEQ/barrel yields annual emissions of 2.11 g I-TEQ_{DF} in 1987 (2.21 g TEQ_{DF}-WHO_{98}) and 2.14 g I-TEQ_{DF} in 1995 (2.24 g TEQ_{DF}-WHO_{98}).

5.4. CIGARETTE SMOKING

Bumb et al. (1980) were the first to report that cigarette smoking is a source of CDD emissions. Subsequent studies by Muto and Takizawa (1989), Ball et al. (1990), and Löfroth and Zebühr (1992) also reported the presence of CDDs as well as CDFs in cigarette smoke. A recent study by Matsueda et al. (1994) reported the CDD/CDF content of the tobacco from 20 brands of cigarettes from seven countries. Although a wide range in the concentrations of total CDD/CDFs and total TEQs were reported in these studies, similar congener profiles and patterns were reported. The findings of each of these studies are described in this section.

No studies published to date have demonstrated a mass balance, and it is not known whether the CDD/CDFs measured in cigarette smoke are the result of formation during tobacco combustion, volatilization of CDD/CDFs present in the unburned tobacco, or a combination of these two source mechanisms. The combustion processes operating during cigarette smoking are complex and could be used to justify both source mechanisms. As reported by Guerin et al. (1992), during a puff, gas phase temperatures reach 850°C at the core of the firecone, and solid phase temperatures reach 800°C at the core and 900°C or greater at the char line. Thus, temperatures are sufficient to cause at least some destruction of CDD/CDFs initially present in the tobacco. Both solid and gas phase temperatures rapidly decline to 200 to 400°C within 2 mm of the char line. Formation of CDD/CDFs has been reported in combustion studies with other media in this temperature range of 200 to 900°C. However, it is known that a process likened by Guerin et al. (1992) to steam distillation takes place in the region behind the char line because of high, localized concentrations of water and temperatures of 200 to 400°C. At least 1,200 tobacco constituents (e.g., nicotine, n-paraffin, some terpenes) are transferred intact from the tobacco into the smoke stream by distillation in this region, and it is plausible that CDD/CDFs present in the unburned tobacco would be subject to similar distillation.

Bumb et al. (1980), using low-resolution mass spectrometry, analyzed the CDD content of mainstream smoke from the burning of a U.S. brand of unfiltered cigarette. A package of 20 cigarettes was combusted in each of two experiments. Approximately 20 to

30 puffs of 2 to 3 seconds duration were collected from each cigarette on a silica column. Hexa-, hepta-, and octa-CDD were detected at levels of 0.004–0.008, 0.009, and 0.02–0.05 ng/g, respectively.

Muto and Takizawa (1989) employed a continuous smoking apparatus to measure CDD congener concentrations in the mainstream smoke generated from the combustion of one kind of filtered cigarette (brand not reported). The apparatus pulled air at a constant continuous rate (rather than a pulsed rate) through a burning cigarette and collected the smoke on a series of traps (glass fiber filter, polyurethane foam, and XAD-II resin). The CDD content of the smoke, as well as the CDD content of the unburned cigarette and the ash from the burned cigarettes, were also analyzed using low-resolution mass spectrometry. The results are presented in Table 5-3, and the congener group profiles are presented in Figure 5-4. Table 5-3 and Figure 5-4 present the mainstream smoke results on a mass per cigarette basis to enable comparison with the results of other studies. The major CDD congener group that was found was HpCDD, which accounted for 84 percent of total CDDs found in the cigarette, 94 percent of total CDDs found in smoke, and 99 percent of total CDDs found in the ash. The 2,3,7,8-HpCDDs also accounted for the majority of the measured TEQ in the cigarettes and smoke; however, none were measured in the ash. Although no PeCDDs were detected in the cigarette, PeCDDs were detected at low levels in the smoke, indicating probable formation during combustion. On the basis of the similarities in the congener group profiles for the three media, Muto and Takizawa (1989) concluded that most of the CDDs found in the cigarette smoke are the result of volatilization of CDD/CDFs present in the unburned cigarette rather than formation during combustion.

Ball et al. (1990) measured the CDD/CDF content of mainstream smoke for the 10 best-selling German cigarette brands. The international test approach (i.e., 1 puff/min; puff flow rate of 35 mL/2 sec) was employed with an apparatus that smoked 20 cigarettes at a time in three successive batches with a large collection device. The average TEQ content (on both an I-TEQ_{DF} and TEQ_{DF}-WHO_{98} basis) in mainstream smoke for the 10 brands tested, normalized to a mass per cigarette basis, was 0.09 pg/cigarette (i.e., 16.5 times less than the value reported by Muto and Takizawa (1989) for a Japanese cigarette brand). However, the congener group profiles were similar to those reported by Muto and Takizawa (1989) with HpCDD and OCDD the dominant congener groups found.

Löfroth and Zebühr (1992) measured the CDD/CDF content of mainstream and sidestream smoke from one common Swedish cigarette brand. The cigarette brand was labeled as giving 17 mg carbon monoxide, 21 mg tar, and 1.6 mg nicotine. The international test approach (i.e., 1 puff/min; puff flow rate of 35 mL/2 sec) was used, and the smoke was collected on glass fiber filters followed by two polyurethane plugs. The analytical results for mainstream and sidestream smoke are presented in Table 5-4. The TEQ content in mainstream smoke, normalized to a mass per cigarette basis, was 0.90 pg I-TEQ_{DF}/cigarette or 0.96 pg TEQ_{DF}-WHO_{98}/cigarette (i.e., about 2 times less than the value reported by Muto and Takizawa (1989) and 10 times greater than the average value reported by Ball et al. 1990). As was reported by Muto and Takizawa (1989) and Ball et al. (1990), the dominant congener groups were HpCDDs and OCDD; however, HpCDFs were also relatively high compared to the other congener group totals. The sidestream smoke contained 1.96 pg I-TEQ_{DF} per cigarette (2.08 pg TEQ_{DF}-WHO_{98} per cigarette), or twice that of mainstream smoke.

Using high-resolution mass spectrometry, Matsueda et al. (1994) analyzed the CDD/CDF content of tobacco from 20 brands of commercially available cigarettes collected in 1992 from Japan, the United States, Taiwan, China, the United Kingdom, Germany, and Denmark. Table 5-5 presents the study results. The total CDD/CDF content and total I-TEQ_{DF} content ranged from 109 to 1,136 pg/pack and from 1.4 to 12.6 pg/pack (1.9 to 14.0 pg/pack on a TEQ_{DF}-WHO_{98} basis), respectively. The Chinese cigarette brand contained significantly lower CDD/CDFs and TEQs than any other brand of cigarette. Figure 5-6 depicts the congener group profiles for the average results for each country. A high degree of similarity is shown in the CDF congener group profiles between the tested cigarette brands. The Japanese and Taiwanese cigarettes show CDD congener group profiles different from the other countries' cigarettes.

In 1995, approximately 487 billion cigarettes were consumed in the United States and by U.S. overseas armed forces personnel. In 1987, approximately 575 billion cigarettes were consumed. Per capita U.S. cigarette consumption, based on total U.S. population aged 16 and over, declined to 2,415 in 1995; the record high was 4,345 in 1963 (The Tobacco Institute, 1995; USDA, 1997). These activity level estimates are assigned a high confidence rating.

The available emission factor data presented above provide the basis for two methods of estimating the amount of TEQs that may have been released to the air in the United States in 1995 and in 1987 from the combustion of cigarettes. The confidence rating assigned to the emission factor is low because of the very limited amount of testing performed to date. First, an annual emission estimate for 1995 of 0.21 g TEQ (on an I-TEQ_{DF} or TEQ_{DF}-WHO_{98} basis) is obtained if it is assumed that (a) the average TEQ content of seven brands of U.S. cigarettes reported by Matsueda et al. (1994), 8.6 pg I-TEQ_{DF}/pack or 8.8 pg TEQ_{DF}-WHO_{98}/pack, are representative of cigarettes smoked in the United States; (b) CDD/CDFs are not formed, and the congener profile reported by Matsueda et al. (1994) is not altered during combustion of cigarettes; and (c) all CDD/CDFs contributing to the TEQ are released from the tobacco during smoking. The second method of estimating is based on the assumption that the TEQ emission rates for a common Swedish brand of cigarette reported by Löfroth and Zebühr (1992) for mainstream smoke (0.90 pg I-TEQ_{DF}/cigarette or 0.96 pg TEQ_{DF}-WHO_{98}/cigarette) and sidestream smoke (1.96 pg I-TEQ_{DF}/cigarette or 2.08 pg TEQ_{DF}-WHO_{98}/cigarette) are representative of the emission rates for U.S. cigarettes. This second method yields an annual emission estimate of 1.41 g I-TEQ_{DF} or 1.48 g TEQ_{DF}-WHO_{98}. For 1987, the two methods yield estimates of 0.25 g TEQ (I-TEQ_{DF} or TEQ_{DF}-WHO_{98} basis) and 1.67 g I-TEQ_{DF} (or 1.75 g TEQ_{DF}-WHO_{98}).

For purposes of this report, the best estimates of annual emissions are assumed to be the average of the annual emissions estimated by the two methods for 1995 and 1987 (0.8 g TEQ and 1.0 g TEQ), respectively (I-TEQ_{DF} or TEQ_{DF}-WHO_{98} basis). Although these emission quantities are relatively small when compared to the emission quantities estimated for various industrial combustion source categories, the emissions are significant because humans are directly exposed to cigarette smoke.

5.5. PYROLYSIS OF BROMINATED FLAME RETARDANTS

The pyrolysis and photolysis of brominated phenolic derivatives and polybrominated biphenyl ethers used as flame retardants in plastics (especially those used in electronic devices), textiles, and paints can generate considerable amounts of polybrominated dibenzo-p-dioxins (BDDs) and dibenzofurans (BDFs) (Watanabe and Tatsukawa, 1987; Thoma and Hutzinger, 1989; Luijk et al., 1992). Watanabe and Tatsukawa (1987) observed the formation of BDFs from the photolysis of decabromobiphenyl ether.

Approximately 20 percent of the decabromobiphenyl ether was converted to BDFs in samples that were irradiated with ultraviolet light for 16 hours.

Thoma and Hutzinger (1989) observed the formation of BDFs during combustion experiments with polybutylene-terephthalate polymers containing 9 to 11 percent decabromodiphenyl ether. Maximum formation of BDFs occurred at 400 to 600°C, with a BDF yield of 16 percent. Although Thoma and Hutzinger (1989) did not provide specific quantitative results for similar experiments conducted with octabromodiphenyl ether and 1,2-bis(tri-bromophenoxy)ethane, they did report that BDDs and BDFs were formed.

Luijk et al. (1992) studied the formation of BDD/BDFs during the compounding and extrusion of decabromodiphenyl ether into high-impact polystyrene polymer at 275°C. HpBDF and OBDF were formed during repeated extrusion cycles, and the yield of BDFs increased as a function of the number of extrusion cycles. HpBDF increased from 1.5 to 9 ppm (in the polymer matrix), and OBDF increased from 4.5 to 45 ppm after four extrusion cycles.

Insufficient data are available at this time from which to derive annual BDD/BDF emission estimates for this source.

5.6. CARBON REACTIVATION FURNACES

Granular activated carbon (GAC) is an adsorbent that is widely used to remove organic pollutants from wastewater and to treat finished drinking water at water treatment plants. Activated carbon is manufactured from the pyrolytic treatment of nut shells and coal (Buonicore, 1992a). The properties of GAC make it ideal for adsorbing and controlling vaporous organic and inorganic chemicals entrained in combustion plasmas, as well as soluble organic contaminants in industrial effluents and drinking water. The high ratio of surface area to particle weight (600 to 1,600 m^2/g), combined with the extremely small pore diameter of the particles (15–25 angstroms), increases the adsorption characteristics (Buonicore, 1992a). GAC eventually becomes saturated, and the adsorption properties significantly degrade. When saturation occurs, GAC usually must be replaced and discarded, which significantly increases the costs of pollution control. The introduction of carbon reactivation furnace technology in the mid-1980s created a method involving the thermal treatment of used GAC to thermolytically desorb the synthetic compounds and restore the adsorption properties for reuse (Lykins et al., 1987). Large-scale regeneration

operations, such as those used in industrial water treatment operations, typically use multiple-hearth furnaces. For smaller-scale operations, such as those used in municipal water treatment operations, fluidized-bed and infrared furnaces are used. Emissions are typically controlled by afterburners followed by water scrubbers (U.S. EPA, 1997b).

The used GAC can contain compounds that are precursors to the formation of CDD/CDFs during the thermal treatment process. EPA measured precursor compounds in spent GAC that was used as a feed material to a carbon reactivation furnace tested during the National Dioxin Study (U.S. EPA, 1987a). The total chlorobenzene content of the GAC ranged from 150 to 6,630 ppb. Trichlorobenzene was the most prevalent species present, with smaller quantities of di- and tetra-chlorobenzenes detected. Total halogenated organics were measured to be about 150 ppm.

EPA has stack-tested two GAC reactivation furnaces for the emission of dioxin (U.S. EPA, 1987a; Lykins et al., 1987). One facility was an industrial carbon reactivation plant, and the second facility was used to restore GAC at a municipal drinking water plant. EPA (1997b) also reported results of other testing performed at a county water facility in California during 1990.

The industrial carbon reactivation plant processed 36,000 kg/day of spent GAC used in the treatment of industrial wastewater effluents. This facility was chosen for testing because it was considered to be representative of other facilities in the source category (U.S. EPA, 1987a). Spent carbon was reactivated in a multiple-hearth furnace, cooled in a water quench, and shipped back to primary chemical manufacturing facilities for reuse. The furnace was fired by natural gas and consisted of seven hearths arranged vertically in series. The hearth temperatures ranged from 480 to 1,000°C. Air pollutant emissions were controlled by an afterburner, a sodium spray cooler, and a fabric filter. Temperatures in the afterburner were about 930°C. The estimated I-TEQ_{DF} emission factor (treating not-detected values as zero) was 0.64 ng I-TEQ_{DF}/kg carbon processed (0.76 ng TEQ_{DF}-WHO_{98}). The emission factor for total CDD/CDF was 58.6 ng/kg. Because analyses were performed only for 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD, and OCDF and the congener groups, equivalent concentrations were assumed for all toxic and nontoxic congeners in each of the penta-, hexa-, and hepta-congener groups.

The second GAC reactivation facility tested by EPA consisted of a fluidized-bed furnace located at a municipal drinking water treatment plant (Lykins et al., 1987). The

furnace was divided into three sections: a combustion chamber, a reactivation section, and a dryer section. The combustion section was fired by natural gas and consisted of a stoichiometrically balanced stream of fuel and oxygen. Combustion temperatures were about 1,038°C. Gases from the reactivation and combustion section were directed through an acid gas scrubber and high-temperature afterburner prior to discharge from a stack. Although measurable concentrations of dioxin-like compounds were detected in the stack emissions, measurements of the individual CDD/CDF congeners were not performed; therefore, it was not possible to derive TEQ emission factors for this facility. With the afterburner operating, no CDD congeners below HpCDD were detected in the stack emissions. Concentrations of HpCDDs and OCDD ranged from 0.001 to 0.05 ppt/v and 0.006 to 0.28 ppt/v, respectively. All CDF congener groups were detected in the stack emissions even with the afterburner operating. Total CDFs emitted from the stack averaged 0.023 ppt/v.

From the results of a test of the reactivation unit at a county water facility in California in 1990, EPA reported a TEQ emission factor of 1.73 ng I-TEQ_{DF}/kg of carbon processed (U.S. EPA, 1997b). The emission factor for total CDD/CDF was reported to be 47 ng/kg (i.e., similar to the total CDD/CDF emission factor of 58.6 ng/kg at the industrial GAC facility). Because congener-specific results were not reported, it was not possible to calculate the TEQ_{DF}-WHO_{98} emission factor. The report also did not provide the configuration and type of furnace tested; however, it did state that the emissions from the furnace were controlled by an afterburner and a scrubber.

The industrial GAC reaction furnace test data indicate that an average of 0.64 ng I-TEQ_{DF}/kg of GAC may be released. The I-TEQ_{DF} emission rate for the reactivation unit at the county water treatment facility was 1.73 ng I-TEQ_{DF}/kg carbon. Low confidence ratings are given to these emission factors because only two GAC reactivation furnaces were stack-tested and not all congeners were analyzed at the industrial GAC facility.

The mass of GAC that is reactivated annually in carbon reactivation furnaces is not known. However, a rough estimate, to which a low confidence rating is assigned, is the mass of virgin GAC shipped each year by GAC manufacturers. According to the Department of Commerce (1990c), 48,000 metric tons of GAC were shipped in 1987. EPA (1995c; 1997b) reported that in 1990, water and wastewater treatment operations

consumed 65,000 metric tons of GAC. The 1990 activity level is used in this document as a surrogate for the 1995 activity level.

Applying the average TEQ emission factor of 1.2 ng I-TEQ_{DF} (or TEQ_{DF}-WHO_{98}) per kg of reactivated carbon for the two tested facilities to the estimates of potential GAC reactivation volumes, yields annual release estimates of 0.06 g I-TEQ_{DF} (or TEQ_{DF}-WHO_{98}) in 1987 and 0.08 g I-TEQ_{DF} (or TEQ_{DF}-WHO_{98}) in 1995 (assuming that the activity level for 1990 is representative of the 1995 activity level).

5.7. KRAFT BLACK LIQUOR RECOVERY BOILERS

Kraft black liquor recovery boilers are associated with the production of pulp in the making of paper using the Kraft process. In this process, wood chips are cooked in large vertical vessels called digesters at elevated temperatures and pressures in an aqueous solution of sodium hydroxide and sodium sulfide. Wood is broken down into two phases: a soluble phase containing primarily lignin, and an insoluble phase containing the pulp. The spent liquor (called black liquor) from the digester contains sodium sulfate and sodium sulfide, which the industry recovers for reuse in the Kraft process. In the recovery of black liquor chemicals, weak black liquor is first concentrated in multiple-effect evaporators to about 65 percent solids. The concentrated black liquor also contains 0.5 to 4 percent chlorides by weight, which are recovered through combustion. The concentrated black liquor is sprayed into a Kraft black liquor recovery furnace equipped with a heat recovery boiler. The bulk of the inorganic molten smelt that forms in the bottom of the furnace contains sodium carbonate and sodium sulfide in a ratio of about 3:1. The combustion gas is usually passed through an electrostatic precipitator (ESP) that collects particulate matter prior to being vented out the stack. The particulate matter can be processed to further recover and recycle sodium sulfate (Someshwar and Pinkerton, 1992).

In 1987, EPA stack-tested three Kraft black liquor recovery boilers for the emission of dioxin in conjunction with the National Dioxin Study (U.S. EPA, 1987a). The three sites tested by EPA were judged to be typical of Kraft black liquor recovery boilers at that time. During pretest surveys, two facilities were judged to have average potential and one was judged to have high potential for CDD/CDF emissions based on the amount of chlorine found in the feed to these units. Dry-bottom ESPs controlled emissions from two of the boilers; a wet-bottom ESP controlled emissions from the third. The results of these tests

include congener group concentrations but lack measurement results for specific congeners other than 2,3,7,8-TCDD and 2,3,7,8-TCDF. NCASI (1995) provided congener-specific emission test results for six additional boilers tested during 1990 to 1993. Three boilers were of the direct contact type, and three were noncontact type. All were equipped with ESPs. The average congener and congener group emission factors are presented in Table 5-6 for the three facilities from U.S. EPA (1987a) and the six facilities from NCASI (1995). Figure 5-7 presents the average congener and congener group profiles based on the test results presented in NCASI (1995).

The average TEQ emission factor based on the data for the six NCASI facilities with complete congener data is 0.029 ng I-TEQ_{DF}/kg of black liquor solids, assuming nondetected values are zero (0.028 ng TEQ_{DF}-WHO_{98}/kg), and 0.068 ng I-TEQ_{DF}/kg assuming nondetected values are present at one-half the detection limit (0.078 ng TEQ_{DF}-WHO_{98}/kg). The results for the three facilities reported in U.S. EPA (1987a) were not used in the derivation of the TEQ emission factor because congener-specific measurements for most 2,3,7,8-substituted congeners were not made in the study. A medium confidence rating is assigned to those emission factors because the emission factors were derived from the stack-testing of six Kraft black liquor recovery boilers that were judged to be fairly representative of technologies used at Kraft pulp mills in the United States. A 1995 survey of the industry indicated that 215 black liquor recovery boilers were in operation at U.S. pulp and paper mills. All but one of these boilers used ESPs for control of particulate emissions; the one unique facility used dual scrubbers. In addition, ESPs were reported to have been the predominant means of particulate control at recovery boilers for the past 20 years (Gillespie, 1998).

The amounts of black liquor solids burned in Kraft black liquor recovery boilers in the United States during 1987 and 1995 were 69.8 million metric tons and 80.8 million metric tons, respectively (American Paper Institute, 1992; American Forest & Paper Association, 1997). These activity level estimates are assigned a high confidence rating because they are based on recent industry survey data. Combining the emission factors derived above with the activity level estimates of 69.8 and 80.8 million metric tons in 1987 and 1995, respectively, yields estimated annual emissions from this source of approximately 2.0 g I-TEQ_{DF} (2.0 g TEQ_{DF}-WHO_{98}) in 1987 and 2.3 g I-TEQ_{DF} (2.3 g TEQ_{DF}-WHO_{98}) in 1995.

5.8. OTHER IDENTIFIED SOURCES

Several manufacturing processes are identified as potential sources of CDD/CDF formation because the processes use chlorine-containing components or involve application of high temperatures. However, no testing of emissions from these processes has been performed in the United States, and only minimal emission rate information has been reported for these processes in other countries.

Burning of Candles. Schwind et al. (1995) analyzed the wicks and waxes of uncolored candles, as well as the fumes of burning candles, for CDD/CDF, total chlorophenol, and total chlorobenzene content. The results presented in Table 5-7 show that beeswax contained the highest levels of CDD/CDF and total chlorophenols. In contrast, the concentration of total chlorobenzenes in stearin wax was higher by a factor of 2 to 3 times than that in paraffin or beeswax. The concentrations of the three analyte groups were significantly lower in the wicks than in the waxes. Emissions of CDD/CDF from all three types of candles were very low during burning. In fact, comparison of the emission factor to the original CDD/CDF concentration in the wax indicates a net destruction of the CDD/CDF originally present in the wax.

Information is not readily available on the volume of candles consumed annually in the United States. However, in 1992, the value of wholesale shipments of candles in the United States was nearly $360 million (U.S. DOC, 1996). Assuming that the average wholesale cost per kg of candle is $1, then the volume of candles shipped was 360 million kg. If it is further assumed that 75 percent of the candle volume is actually burned and that the CDD/CDF emissions rate is 0.015 ng/kg, then a rough preliminary estimate of the potential annual emission from combustion of candles is 4 mg I-TEQ_{DF}/yr.

Glass Manufacturing. Bremmer et al. (1994) and Douben et al. (1995) estimated annual emissions of less than 1 g I-TEQ_{DF}/yr from glass manufacturing facilities in The Netherlands and the United Kingdom, respectively. Glass is manufactured by heating a mixture of sand and, depending on the type of glass, lime, sodium carbonate, dolomite, clay, or feldspar to a temperature of 1,400 to 1,650°C. In addition, various coloring and clarifying agents may be added. Chlorine enters the process as a contaminant (i.e., NaCl) in sodium carbonate (Bremmer et al. 1994). However, the emission factors used by Bremmer et al. (1994) and Douben et al. (1995) were not reported. Umweltbundesamt

(1996) reported relatively low emission factors (approximately 0.002 and 0.007 ng I-TEQ_{DF}/kg) for two glass manufacturing facilities in Germany.

Lime Kilns. Annual emissions from lime kilns in Belgium and the United Kingdom have been reported by Wevers and De Fre (1995) and Douben et al. (1995), respectively. However, the emission factors used to generate those estimates were not provided. Umweltbundesamt (1996) reported low emissions (0.016 to 0.028 ng I-TEQ_{DF}/kg) during tests at two lime kilns in Germany.

Ceramics and Rubber Manufacturers. Douben et al. (1995) estimated annual emissions from ceramic manufacturers and rubber manufacturers in the United Kingdom. Lexen et al. (1993) had previously detected high concentrations of CDD/CDF in emissions from a ceramic manufacturer in Sweden, which occasionally glazed ceramics by volatilization of sodium chloride in a coal-fired oven. Lexen et al. (1993) also detected high pg/L levels of I-TEQ_{DF} in the scrubber water from the vulcanization process at a Swedish rubber manufacturer.

Table 5-1. CDD/CDF Emission Factors for Cement Kilns

Congener/Congener Group	Kilns Burning Hazardous Waste—Mean Emission Factor (ND values set equal to zero) (ng/kg clinker produced)		Kilns Not Burning Hazardous Waste—Mean Emission Factor (ND values set equal to zero) (ng/kg clinker produced)
	APCD Inlet Temperature > 450°F	APCD Inlet Temperature < 450°F	
2,3,7,8-TCDD	3.38	0.02	0.012
1,2,3,7,8-PeCDD	4.28	0.13	0.034
1,2,3,4,7,8-HxCDD	4.85	0.29	0.028
1,2,3,6,7,8-HxCDD	6.93	0.42	0.042
1,2,3,7,8,9-HxCDD	9.55	0.40	0.048
1,2,3,4,6,7,8-HpCDD	27.05	3.16	0.426
OCDD	18.61	1.08	0.692
2,3,7,8-TCDF	36.26	3.24	0.729
1,2,3,7,8-PeCDF	13.36	0.23	0.102
2,3,4,7,8-PeCDF	23.48	0.65	0.224
1,2,3,4,7,8-HxCDF	22.24	0.55	0.185
1,2,3,6,7,8-HxCDF	8.46	0.27	0.054
1,2,3,7,8,9-HxCDF	0.96	0.06	0.007
2,3,4,6,7,8-HxCDF	13.33	0.52	0.082
1,2,3,4,6,7,8-HpCDF	7.73	0.34	0.146
1,2,3,4,7,8,9-HpCDF	2.16	0.16	0.005
OCDF	2.51	0.37	0.234
Total I-TEQ_{DF}	28.58	1.04	0.27
Total TEQ_{DF}-WHO_{98}	30.70	1.11	0.29
Total TCDD	406.76	1.78	1.97
Total PeCDD	608.65	0.89	2.07
Total HxCDD	845.99	0.69	5.96
Total HpCDD	192.99	0.42	0.84
Total OCDD	18.61	1.08	0.69
Total TCDF	295.72	11.52	6.82
Total PeCDF	127.99	3.83	2.00
Total HxCDF	50.75	1.88	0.60
Total HpCDF	8.36	0.47	0.24
Total OCDF	2.51	0.37	0.23
Total CDD/CDF	2558.33	22.92	21.44

NR = Not reported.

Source: U.S. EPA (1996c)

Table 5-2. CDD/CDF Emission Factors for Petroleum Catalytic Reforming Units

Congener/Congener Group	Semi-regenerative Unit (ng/barrel)		Continuous Regeneration Unit (ng/barrel)	
	Nondetects Set to Zero	Nondetects Set to ½ Det. Limit	Nondetects Set to Zero	Nondetects Set to ½ Det. Limit
2,3,7,8-TCDD	ND	2.35e-05	1.61e-02	1.61e-02
1,2,3,7,8-PeCDD	5.69e-05	9.58e-05	2.87e-01	2.87e-01
1,2,3,4,7,8-HxCDD	4.22e-05	8.09e-05	3.47e-01	3.47e-01
1,2,3,6,7,8-HxCDD	ND	5.52e-05	8.45e-01	8.45e-01
1,2,3,7,8,9-HxCDD	ND	5.10e-05	5.56e-01	5.56e-01
1,2,3,4,6,7,8-HpCDD	7.02e-04	7.02e-04	3.02e+00	3.02e+00
OCDD	2.55e-03	2.55e-03	1.71e+00	1.71e+00
2,3,7,8-TCDF	2.32e-04	2.32e-04	6.10e-01	6.10e-01
1,2,3,7,8-PeCDF	4.68e-04	4.68e-04	1.72e+00	1.72e+00
2,3,4,7,8-PeCDF	1.09e-03	1.09e-03	2.33e+00	2.33e+00
1,2,3,4,7,8-HxCDF	1.06e-03	1.06e-03	4.70e+00	4.70e+00
1,2,3,6,7,8-HxCDF	1.07e-03	1.07e-03	3.58e+00	3.58e+00
1,2,3,7,8,9-HxCDF	ND	6.82e-05	4.34e-01	4.34e-01
2,3,4,6,7,8-HxCDF	1.24e-03	1.24e-03	3.10e+00	3.10e+00
1,2,3,4,6,7,8-HpCDF	2.94e-03	2.94e-03	1.59e+01	1.59e+01
1,2,3,4,7,8,9-HpCDF	8.32e-04	8.32e-04	1.45e+00	1.45e+00
OCDF	1.01e-03	1.01e-03	3.75e+00	3.75e+00
Total 2,3,7,8-CDD	3.35e-03	3.56e-03	6.77e+00	6.77e+00
Total 2,3,7,8-CDF	9.94e-03	1.00e-02	3.76e+01	3.76e+01
Total I-TEQ_{DF}	1.01e-03	1.08e-03	3.04e+00	3.04e+00
Total TEQ_{DF}-WHO_{98}	1.04e-03	1.12e-03	3.18e+00	3.18e+00
Total TCDD	ND	2.35e-05	6.84e+00	6.84e+00
Total PeCDD	3.56e-04	3.56e-04	5.61e+00	5.61e+00
Total HxCDD	1.28e-03	1.28e-03	8.18e+00	8.18e+00
Total HpCDD	1.39e-03	1.39e-03	6.58e+00	6.58e+00
Total OCDD	2.55e-03	2.55e-03	1.71e+00	1.71e+00
Total TCDF	2.70e-03	2.70e-03	4.68e+01	4.68e+01
Total PeCDF	5.12e-03	5.12e-03	3.30e+01	3.30e+01
Total HxCDF	7.85e-03	7.85e-03	2.96e+01	2.96e+01
Total HpCDF	4.88e-03	4.88e-03	2.11e+01	2.11e+01
Total OCDF	1.01e-03	1.01e-03	3.75e+00	3.75e+00
Total CDD/CDF	2.71e-02	2.72e-02	1.63e+02	1.63e+02

ND = Not detected.

Note: 1 barrel assumed to be equivalent to 139 kg.

Sources: Radian (1991b) and CARB (1999)

Table 5-3. CDD Concentrations in Japanese Cigarettes, Smoke, and Ash

Congener/Congener Group	Cigarette (pg/g)	Concentrations	
		Mainstream Smoke (ng/m^3)	Ash (pg/g)
2,3,7,8-TCDD	ND (0.5)	ND (0.22)	ND (0.5)
1,2,3,7,8-PeCDD	ND (0.5)	0.43	ND (0.5)
1,2,3,4,7,8-HxCDD	2.01[a]	2.15[a]	0.56[a]
1,2,3,6,7,8-HxCDD	a	a	a
1,2,3,7,8,9-HxCDD	a	a	a
1,2,3,4,6,7,8-HpCDD	1,343	783	ND (0.5)
OCDD	257	240	ND (0.5)
2,3,7,8-TCDF	—	—	—
1,2,3,7,8-PeCDF	—	—	—
2,3,4,7,8-PeCDF	—	—	—
1,2,3,4,7,8-HxCDF	—	—	—
1,2,3,6,7,8-HxCDF	—	—	—
1,2,3,7,8,9-HxCDF	—	—	—
2,3,4,6,7,8-HxCDF	—	—	—
1,2,3,4,6,7,8-HpCDF	—	—	—
1,2,3,4,7,8,9-HpCDF	—	—	—
OCDF	—	—	—
Total 2,3,7,8-CDD	1,602	1,026	0.56
Total 2,3,7,8-CDF	--	--	--
Total I-TEQ_{DF}	13.9	8.5	0.06
Total TEQ_{DF}-WHO_{98}	13.7	8.3	0.06
Total TCDD	44.9	68.0	4.63
Total PeCDD	ND (0.5)	1.51	ND (0.5)
Total HxCDD	13.41	7.51	5.01
Total HpCDD	1,629	4,939	3,211
Total OCDD	257	240	ND (0.5)
Total TCDF	—	—	—
Total PeCDF	—	—	—
Total HxCDF	—	—	—
Total HpCDF	—	—	—
Total OCDF	—	—	—
Total CDD/CDF	1,944	5,256	3,221

ND = Not detected (detection limit is in parentheses).
— = Not reported.

a Value reported only for total 2,3,7,8-substituted HxCDDs.

Source: Muto and Takizawa (1989)

Table 5-4. CDD/CDF Emissions in Cigarette Smoke

Congener/Congener Group	Concentrations — Normalized to a per Cigarette Basis (pg/cig)			
	Ref. A (1 Japanese brand) (mainstream smoke)	Ref. B (Avg of 10 German brands) (mainstream smoke)	Ref. C (1 Swedish brand) (mainstream smoke)	Ref. C (1 Swedish brand) (sidestream smoke)
2,3,7,8-TCDD	ND (0.04)	ND (0.03)	0.028	0.07
1,2,3,7,8-PeCDD	0.075	ND (0.03)	0.15	0.32
1,2,3,4,7,8-HxCDD	0.376	0.06	0.10	0.19
1,2,3,6,7,8-HxCDD	b	0.05	0.34	0.60
1,2,3,7,8,9-HxCDD	b	0.04	0.25	0.55
1,2,3,4,6,7,8-HpCDD	137	1.3	6.05	12.2
OCDD	42	3.4	22.1	38.8
2,3,7,8-TCDF	—	0.19	1.2[c]	2.1[c]
1,2,3,7,8-PeCDF	—	0.13	0.34[c]	0.80[c]
2,3,4,7,8-PeCDF	—	0.04	0.34	0.60
1,2,3,4,7,8-HxCDF	—	ND (0.03)	1.3[c]	3.8[c]
1,2,3,6,7,8-HxCDF	—	0.03	0.48	1.2
1,2,3,7,8,9-HxCDF	—	0.03	0.14	0.39
2,3,4,6,7,8-HxCDF	—	0.05	0.21	0.50
1,2,3,4,6,7,8-HpCDF	—	0.16	10.0	23.5
1,2,3,4,7,8,9-HpCDF	—	0.03	2.6	5.0
OCDF	—	0.11	3.2	10.7
Total 2,3,7,8-CDD	179	4.85	29.0	52.7
Total 2,3,7,8-CDF	--	0.77	19.8	48.6
Total I-TEQ_{DF}	1.49	0.09	0.90	1.96
Total TEQ_{DF}-WHO_{98}	1.49	0.09	0.96	2.08
Total TCDD	11.9	0.51	0.61	0.67
Total PeCDD	0.264	0.14	1.07	2.14
Total HxCDD	1.31	0.53	2.52	5.2
Total HpCDD	864	2.9	12.3	21.3
Total OCDD	42	3.4	22.1	38.8
Total TCDF	—	1.41	4.5	5.75
Total PeCDF	—	0.83	3.23	6.35
Total HxCDF	—	0.35	5.30	12.9
Total HpCDF	—	0.27	19.8	47.8
Total OCDF	—	0.11	3.2	10.7
Total CDD/CDF	919	10.5	74.5	152

Ref. A: Muto and Takizawa (1989)
Ref. B: Ball et al. (1990)
Ref. C: Löfroth and Zebühr (1992)

ND = Not detected (detection limit is in parentheses).
— = Not reported.
a Emissions calculated assuming 0.0035 m^3 of smoke are inhaled per 20 cigarettes smoked (Muto and Takizawa, 1992).
b Ref. A reported a value only for total 2,3,7,8-HxCDDs (0.38 pg/cig).
c Concentrations listed include the contribution of a coeluting non-2,3,7,8-substituted congener.

Table 5-5. CDD/CDF Concentrations in Cigarette Tobacco

Congener/Congener Group	Concentrations in Brands from Various Countries (pg/pack)						
	U.S. Brands (Avg of 7 brands)	Japan (Avg of 6 brands)	United Kingdom (Avg of 3 brands)	Taiwan (1 brand)	China (1 brand)	Denmark (1 brand)	Germany (1 brand)
2,3,7,8-TCDD	1.2	0.5	1.7	1.0	ND	0.5	1.1
1,2,3,7,8-PeCDD	1.6	1.4	3.1	3.3	1.1	0.8	3.3
1,2,3,4,7,8-HxCDD	6.9	4.8	6.1	12.2	1.1	6.2	5.7
1,2,3,6,7,8-HxCDD	a	a	a	a	a	a	a
1,2,3,7,8,9-HxCDD	a	a	a	a	a	a	a
1,2,3,4,6,7,8-HpCDD	52.7	17.8	23.9	26.4	2.2	53.3	32.7
OCDD	589.3	244.0	189.5	272.7	28.2	354.3	288.6
2,3,7,8-TCDF	18.2	4.8	15.6	11.0	1.2	2.2	7.9
1,2,3,7,8-PeCDF	8.7	5.3	21.2	16.0	1.5	4.3	14.4
2,3,4,7,8-PeCDF	b	b	b	b	b	b	b
1,2,3,4,7,8-HxCDF	8.1	8.1	17.0	12.9	2.2	4.3	13.2
1,2,3,6,7,8-HxCDF	c	c	c	c	c	c	c
1,2,3,7,8,9-HxCDF	c	c	c	c	c	c	c
2,3,4,6,7,8-HxCDF	c	c	c	c	c	c	c
1,2,3,4,6,7,8-HpCDF	17.6	11.1	13.6	13.2	1.5	7.0	12.9
1,2,3,4,7,8,9-HpCDF	d	d	d	d	d	d	d
OCDF	24.6	10.5	8.3	13.9	0.5	10.5	13.9
Total 2,3,7,8-CDD	652	268.5	224.3	315.6	32.6	415.1	331.4
Total 2,3,7,8-CDF	77.2	39.8	75.7	67	6.9	28.3	62.3
Total I-TEQ_{DF}	8.6	4.6	12.6	9.3	1.4	3.8	9.1
Total TEQ_{DF}-WHO_{98}	8.8	5.1	14.0	10.7	1.9	3.9	10.5
Total TCDD	47.1	296.3	85.1	329	9.7	17.0	49.5
Total PeCDD	27.6	33.6	62.9	150.5	5.2	9.8	40.8
Total HxCDD	40.6	29.2	49.2	99.4	5.4	26.7	40.6
Total HpCDD	108.7	40.0	47.7	62.0	3.8	93.1	60.2
Total OCDD	589.3	244.0	189.5	272.7	28.2	354.3	288.6
Total TCDF	183.8	102.1	348.9	372.1	35.4	97.8	233.4
Total PeCDF	57.7	45.9	134.5	149.1	11.2	35.5	97.5
Total HxCDF	29.1	26.4	51.3	45.8	7.8	18.1	40.8
Total HpCDF	27.3	16.6	19.0	18.5	1.7	11.1	21.2
Total OCDF	24.6	10.5	8.3	13.9	0.5	10.5	13.9
Total CDD/CDF	1136	845	996	1513	109	674	887

Source: Matsueda et al. (1994)

a Value reported only for total 2,3,7,8-substituted HxCDDs.
b Value reported only for total 2,3,7,8-substituted PeCDFs.
c Value reported only for total 2,3,7,8-substituted HxCDFs.
d Value reported only for total 2,3,7,8-substituted HpCDFs.

Table 5-6. CDD/CDF Emission Factors for Black Liquor Recovery Boilers

Congener	U.S. EPA (1987) — 3 Facilities Mean Emission Factors (ng/kg feed)		NCASI (1995) — 6 Facilities Mean Emission Factors (ng/kg feed)	
	Nondetects Set to Zero	Nondetects Set to ½ Det. Limit	Nondetects Set to Zero	Nondetects Set to ½ Det. Limit
2,3,7,8-TCDD	0	0.04	0	0.016
1,2,3,7,8-PeCDD	NR	NR	0	0.016
1,2,3,4,7,8-HxCDD	NR	NR	0.001	0.018
1,2,3,6,7,8-HxCDD	NR	NR	0.003	0.015
1,2,3,7,8,9-HxCDD	NR	NR	0.006	0.019
1,2,3,4,6,7,8-HpCDD	NR	NR	0.108	0.135
OCDD	4.24	4.24	1.033	1.054
2,3,7,8-TCDF	0.04	0.06	0.040	0.049
1,2,3,7,8-PeCDF	NR	NR	0.030	0.036
2,3,4,7,8-PeCDF	NR	NR	0.033	0.037
1,2,3,4,7,8-HxCDF	NR	NR	0.007	0.022
1,2,3,6,7,8-HxCDF	NR	NR	0.012	0.021
1,2,3,7,8,9-HxCDF	NR	NR	0.005	0.016
2,3,4,6,7,8-HxCDF	NR	NR	0.010	0.021
1,2,3,4,6,7,8-HpCDF	NR	NR	0.024	0.035
1,2,3,4,7,8,9-HpCDF	NR	NR	0	0.014
OCDF	0.35	0.35	0.113	0.130
Total TCDD	0.21	0.36	0.106	0.123
Total PeCDD	0.27	0.35	0.013	0.059
Total HxCDD	0.80	1.02	0.104	0.122
Total HpCDD	2.05	2.05	0.252	0.279
Total OCDD	4.24	4.24	1.033	1.054
Total TCDF	0.95	1.00	1.270	1.275
Total PeCDF	0.64	0.77	0.370	0.376
Total HxCDF	1.16	1.20	0.102	0.109
Total HpCDF	1.05	1.05	0.024	0.038
Total OCDF	0.35	0.35	0.113	0.130
Total I-TEQ_{DF}	0.10*	0.15*	0.029	0.065
Total TEQ_{DF}-WHO_{98}	0.10*	0.16*	0.028	0.072
Total CDD/CDF	11.71	12.17	3.386	3.566

NR = Not reported.

* Estimated based on the measured data for 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD, and OCDF and congener group emissions (i.e., for the penta-, hexa-, and hepta-CDD and CDFs, it was assumed that the measured emission factor within a congener group was the sum of equal emission factors for all congeners in that group, including non-2,3,7,8-substituted congeners).

Sources: U.S. EPA (1987a); NCASI (1995)

Table 5-7. Concentrations of CDD/CDF in Candle Materials and Emissions

Wax Material	Candle Component	Concentration			Emission Factor
		CDD/CDF (ng I-TEQ_{DF}/kg)	Total Chlorophenols (μg/kg)	Total Chlorobenzenes (μg/kg)	CDD/CDF (ng I-TEQ_{DF}/kg burnt wax)
Paraffin	Wax	0.59	14.8	130	0.015
Stearin	Wax	1.62	32.3	330	0.027
Beeswax	Wax	10.99	256	120	0.004
Paraffin	Wick	0.18	1.23	0.67	—
Stearin	Wick	0.12	0.94	0.34	—
Beeswax	Wick	0.08	0.74	0.35	—

Source: Schwind et al. (1995)

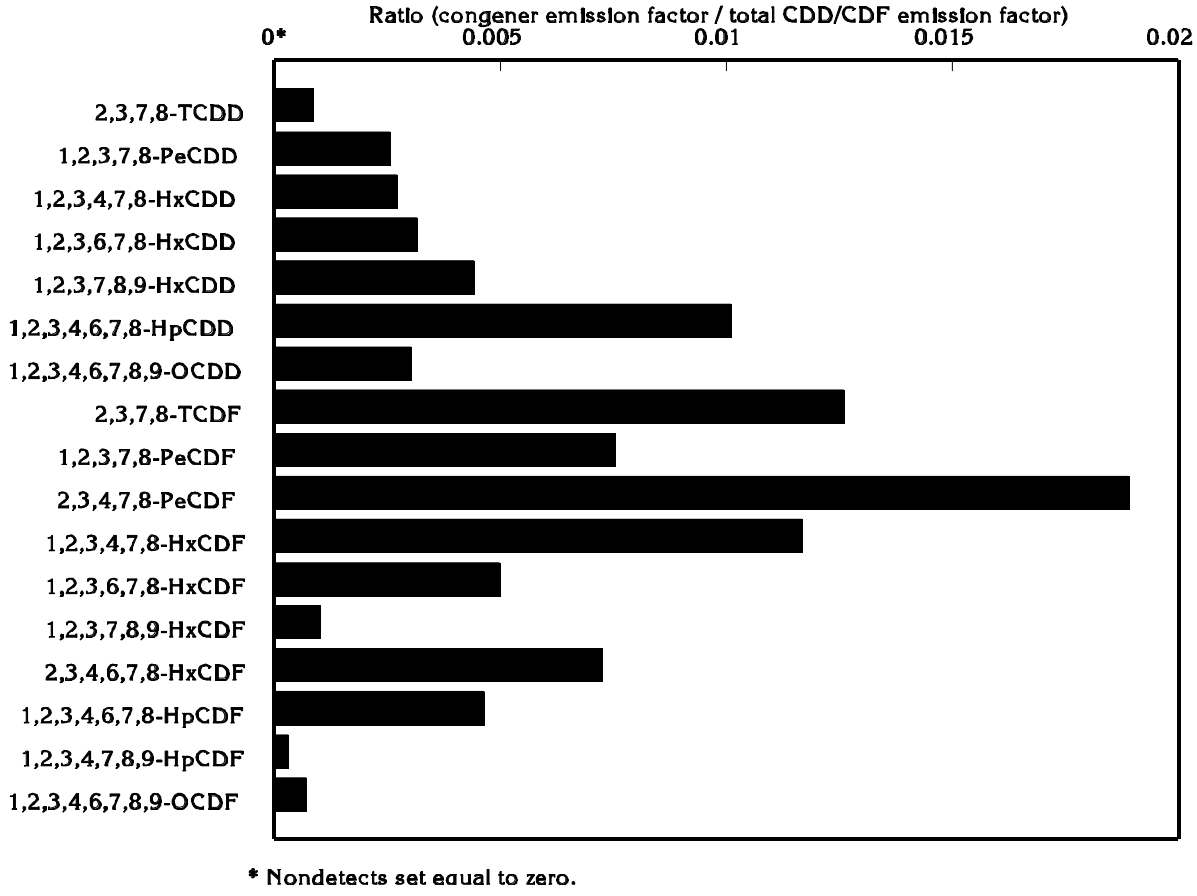


Figure 5-1. Congener Profile for Air Emissions from Cement Kilns Burning Hazardous Waste

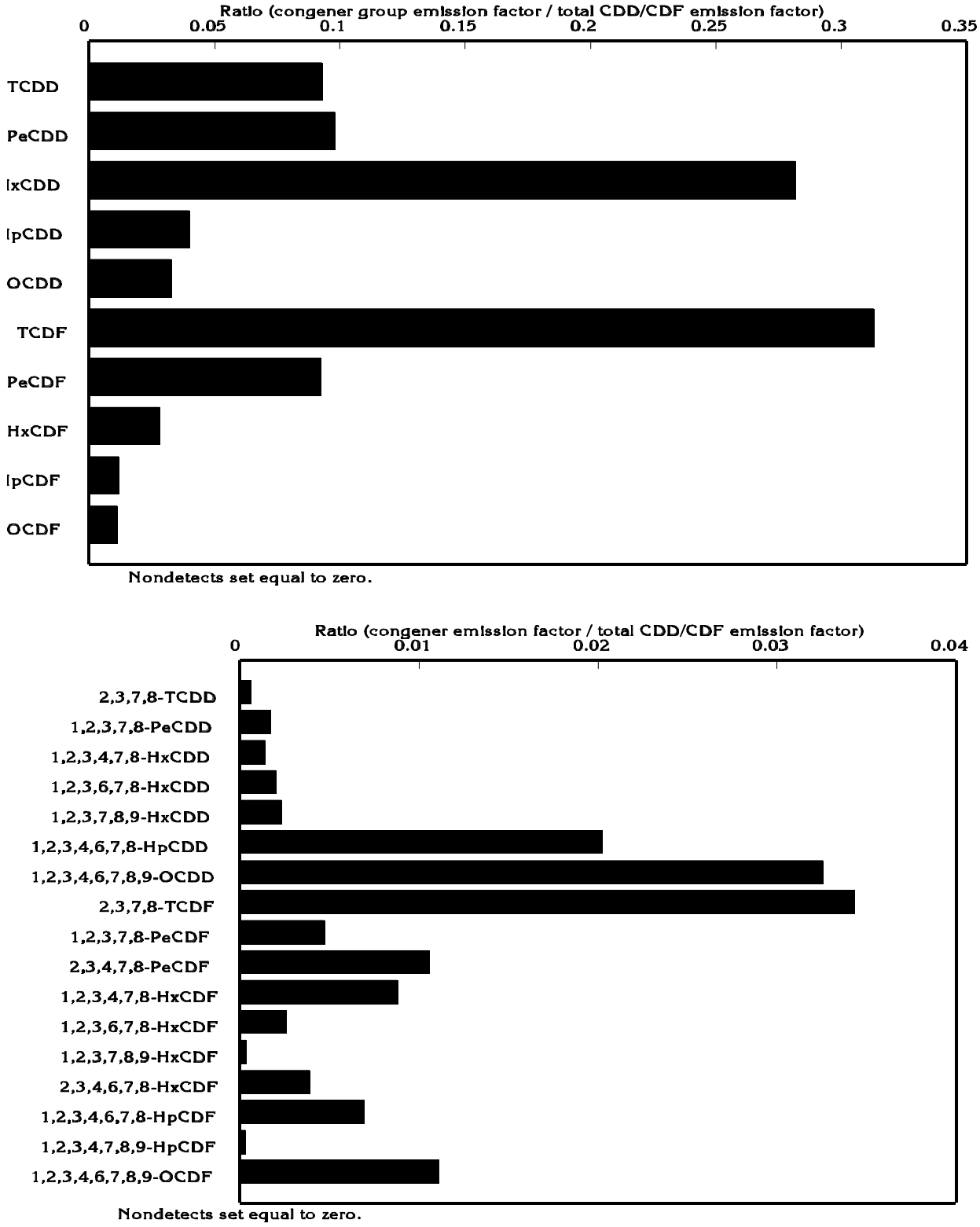


Figure 5-2. Congener and Congener Group Profiles for Air Emissions from Cement Kilns Not Burning Hazardous Waste

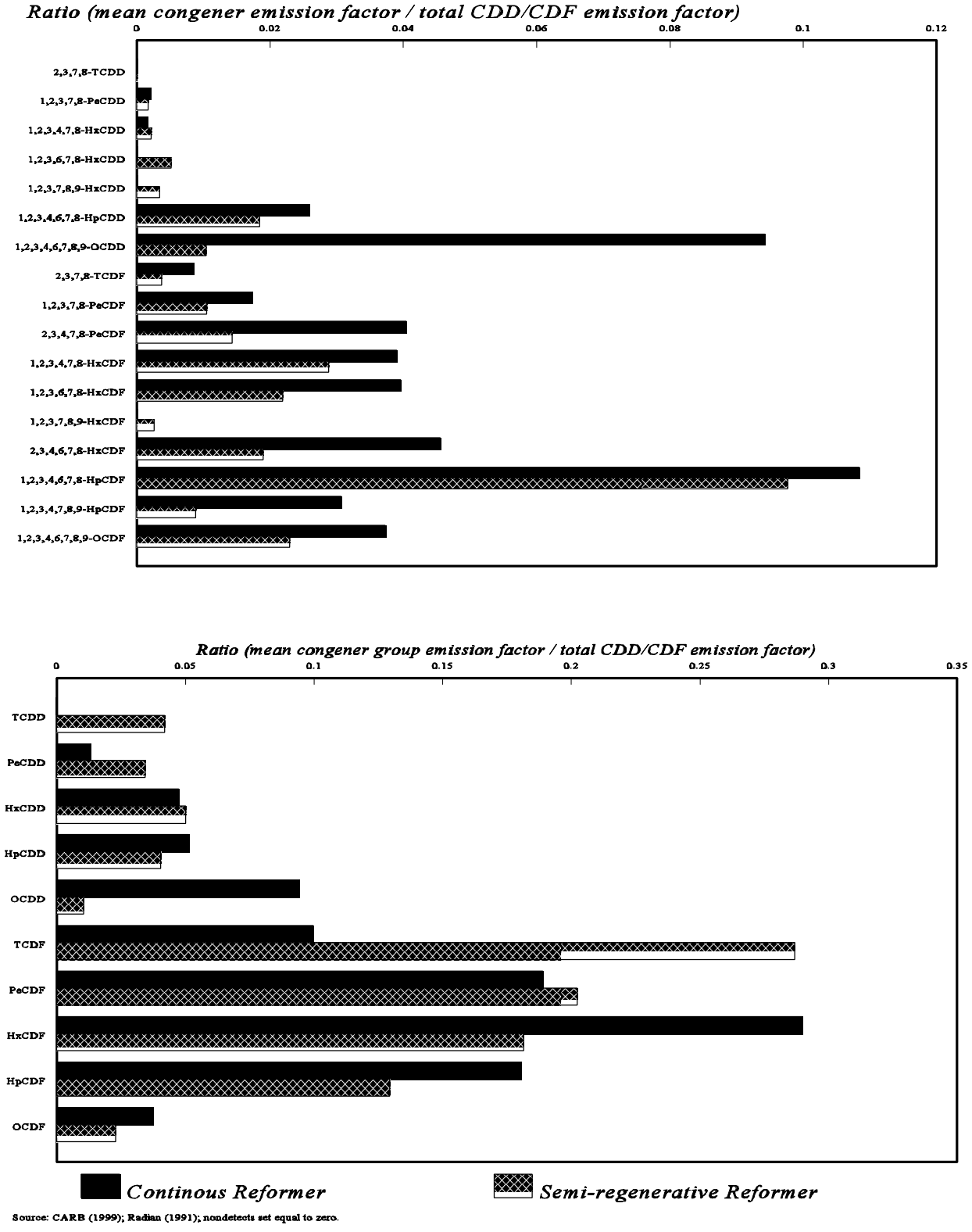


Figure 5-3. Congener and Congener Group Profiles for Air Emissions from Petroleum Catalytic Reforming Units

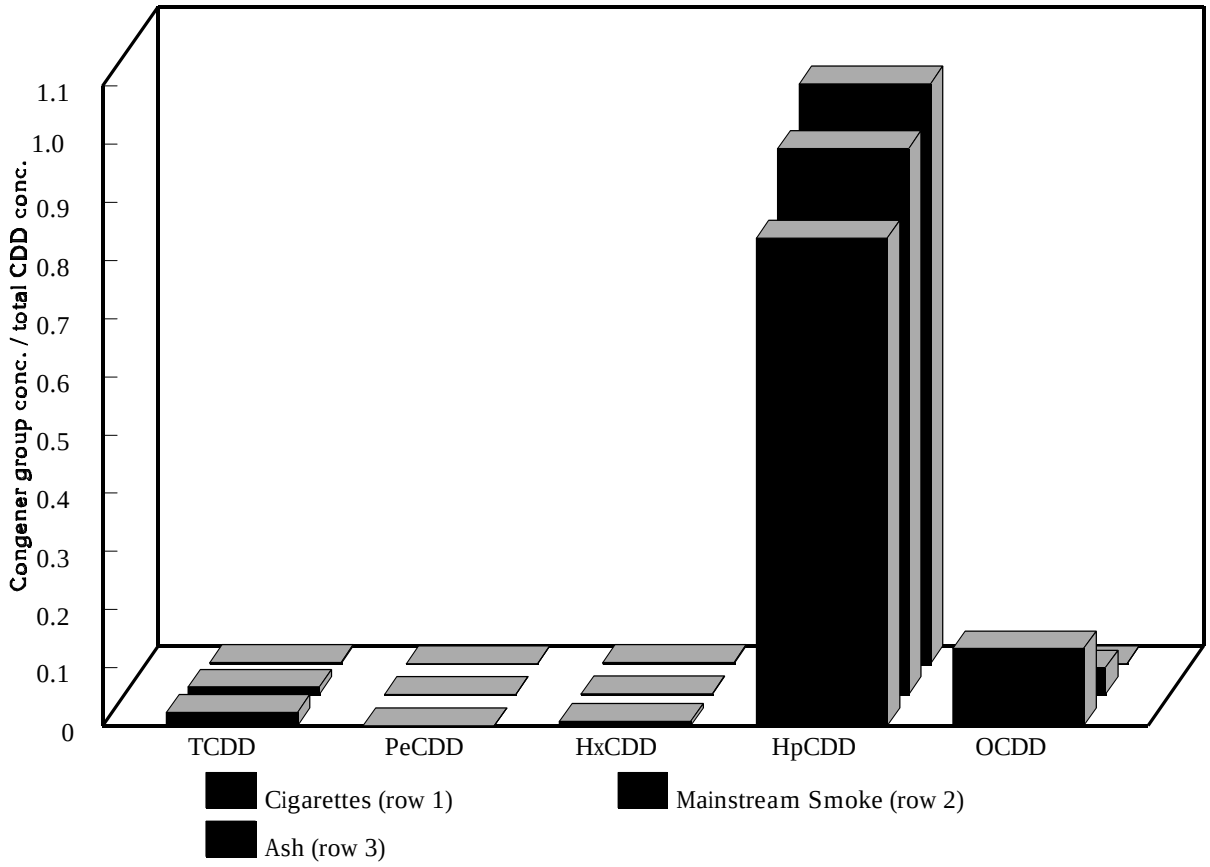


Figure 5-4. CDD Profiles for Japanese Cigarettes, Smoke, and Ash

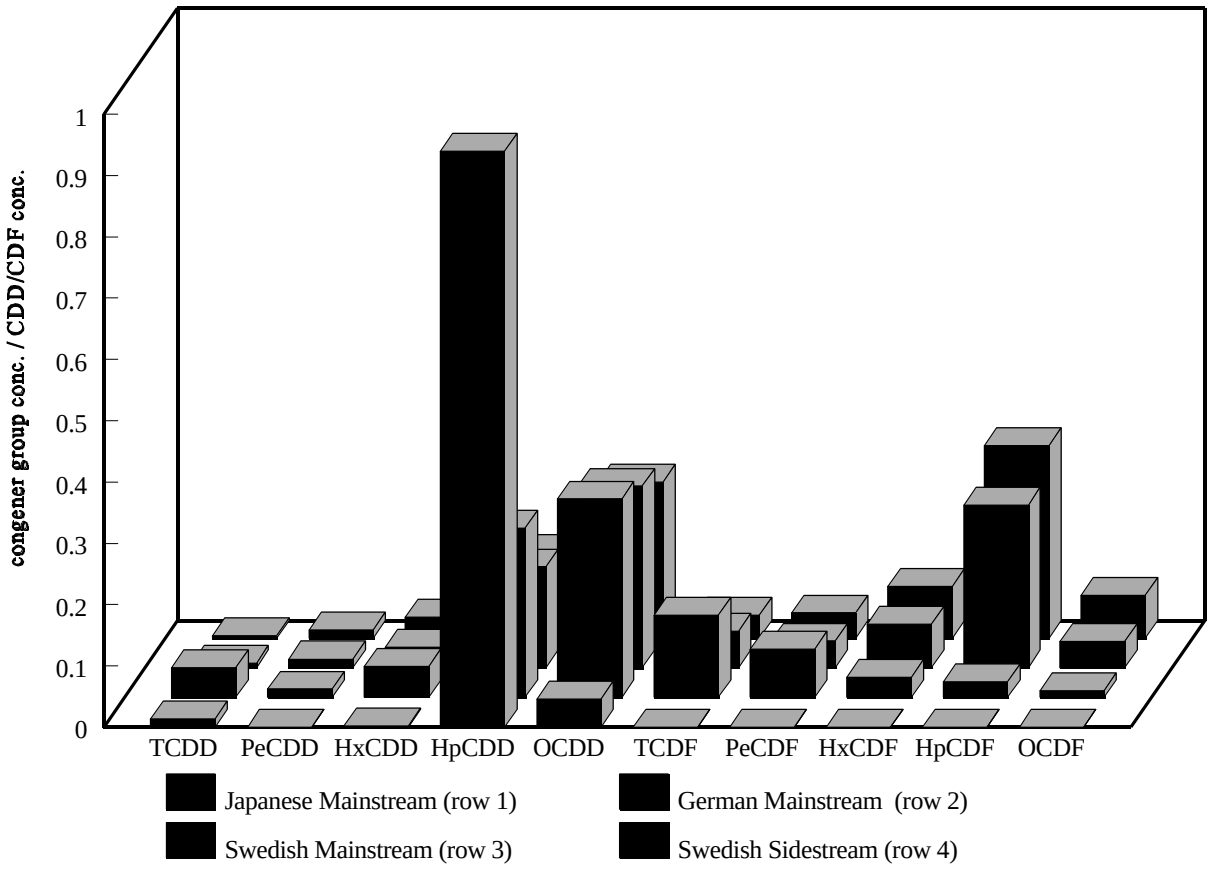
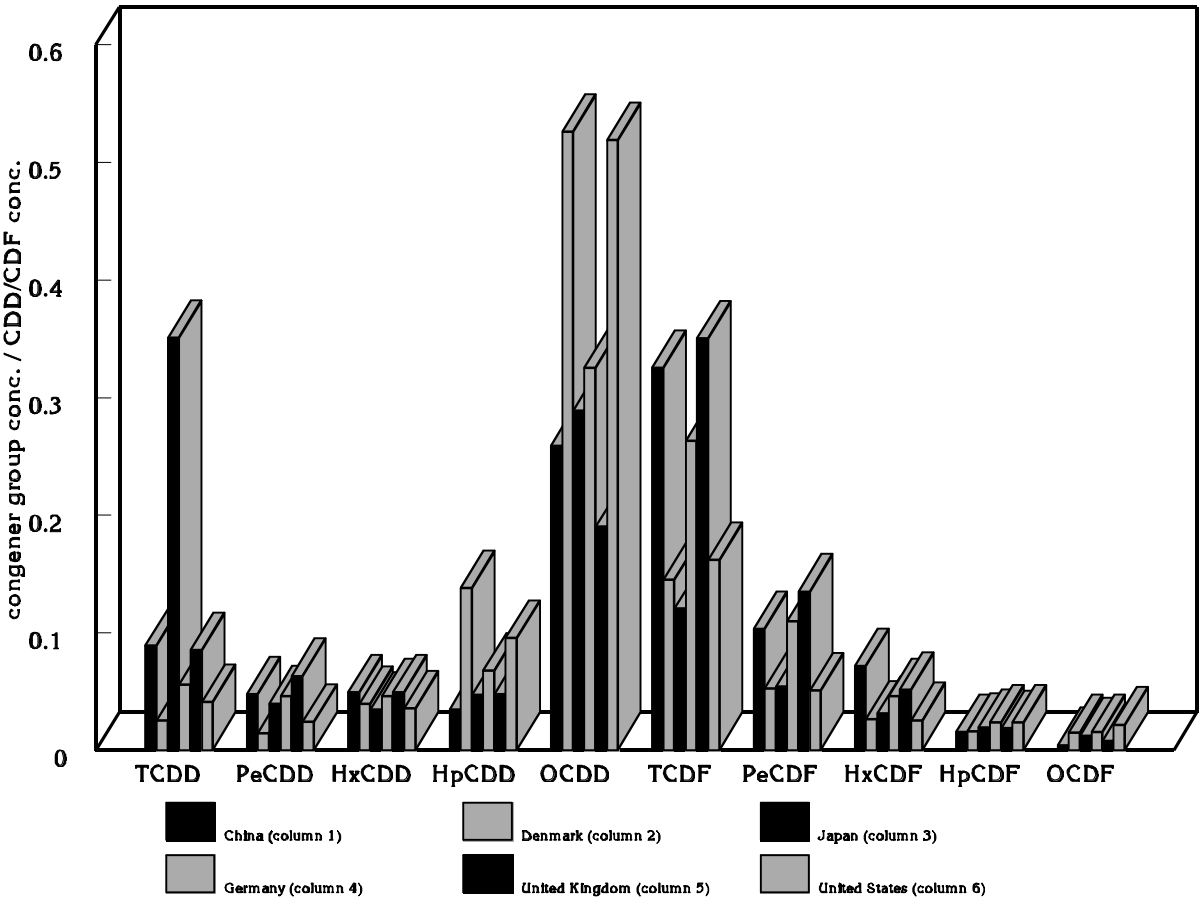


Figure 5-5. Congener Group Profiles for Mainstream and Sidestream Cigarette Smoke



Source: Matsueda et al. (1994)

Figure 5-6. Congener Group Profiles for Cigarette Tobacco from Various Countries

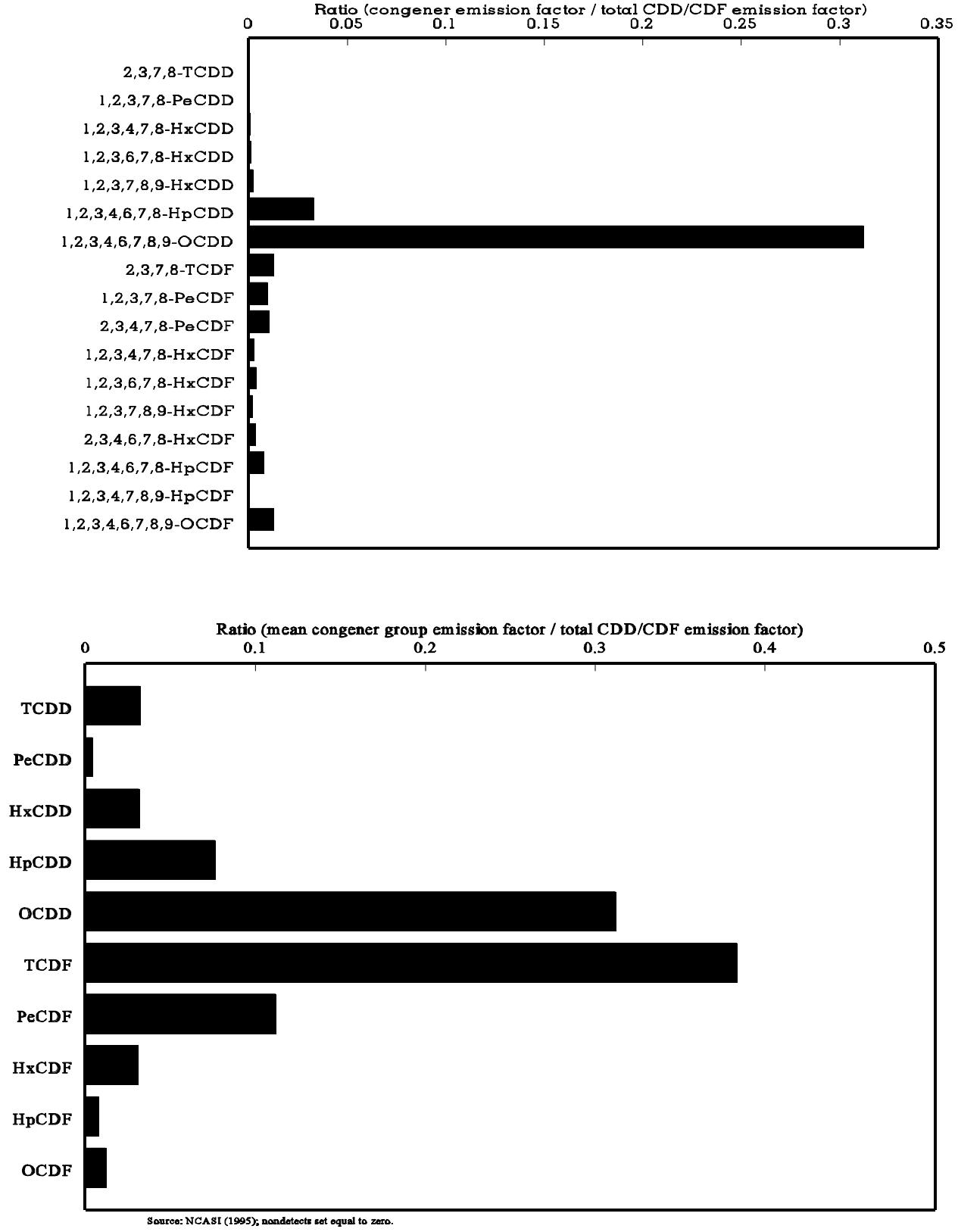


Figure 5-7. Congener and Congener Group Profiles for Air Emissions from Kraft Black Liquor Recovery Boilers